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Section A.—Mathematical and Physical Sciences.

Optical Dispersion: A Comparison of the Maxima of Absorption and Selective Reflection for Certain Substances.

By T. H. Havelock, M.A., D.Sc., Armstrong College, Newcastle-on-Tyne.

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Introduction and Summary.

In the comparison of optical dispersion formulæ with experimental results, it is important to consider the meaning of the various constants, and in particular of the natural wave-lengths which occur in them.

With the formula in the simple form $n^2-1 = \Sigma C_1/(\lambda^2-\lambda_1^2)$, the quantities λ_1 are the wave-lengths of the natural vibrations and have been identified in practice indiscriminately with the wave-length of maximum absorption or that of selective reflection obtained by the method of residual rays. This interpretation is allowable if the absorption is very small. For a more general type of formula such as $(n^2-1)/(n^2+a) = \Sigma C_1/(\lambda^2-\lambda_1^2)$, the corresponding wave-length, on a similar argument, for small absorption is a certain wave-length λ_1', which is larger than λ_1; in a previous paper* numerical examples were given of the difference between the wave-lengths λ_1 and λ_1'. The present paper includes absorption more generally in the formulæ, so as to determine the position of the various maxima more accurately.

Using dispersion formulæ of a general type, an expression is found for the position of the maximum of κ, the coefficient of extinction; further, a quartic equation is obtained, three of whose roots give the maximum of $n\kappa$, and the minimum and maximum of the refractive index n. The next step is to consider numerical examples of these formulæ. We choose first a substance for which the dispersion and absorption have been measured, namely, iodeosin; for this we calculate the positions of the various maxima and compare with experimental results. The remaining examples are carbon disulphide, rock salt, and sodium vapour. For these substances dispersion formulæ are known in a form not involving absorption; the formulæ have been completed by introducing coefficients of suitable value, and the maxima of absorption and of selective reflection have then been determined. The results illustrate the differences that may exist between these wave-lengths and the wave-lengths λ_1 of the simple dispersion formula; in the infra-red especially, where reflective power is large, the maximum of selective reflection is proved in general to be displaced considerably from the natural wave-length λ_1 or from the position of maximum absorption.

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* 'Roy. Soc. Proc.,' A, 1911, vol. 84, p. 512.

Derivation of Formulæ for Maxima.

Although there are various physical theories of the mechanism of absorption, such as those of Lorentz and Planck, the final formulæ are of the same form as those obtained by introducing a simple frictional term into the equation of motion of the vibrating particle.

In terms of frequency p, where the time factor has been made e^{ipt}, the complete dispersion formula is

$$\frac{1}{\sigma+1/(\mathfrak{n}^2-1)} = \Sigma_s \frac{C_s}{p_s^2-p^2+ib_sp}, \tag{1}$$

where $\mathfrak{n} = n(1-i\kappa)$. The quantity σ is a constant: two special types are obtained by making it zero, or $\frac{1}{3}$; p_s is the frequency of the natural undamped vibrations. If we consider the vibrating particle to be of mass m_s and to carry a charge e_s, we have C_s equal to $4\pi N_s e_s^2/m_s$, where N_s is the number of such particles in unit volume.

In what follows we are concerned specially with values of p in the neighbourhood of a frequency p_s. We shall assume that the region of absorption in question is removed from other similar regions, so that in the above summation all the terms except one may be replaced by a quantity independent of p; hence, in the vicinity of a frequency p_1, we write

$$\frac{1}{\sigma+1/(\mathfrak{n}^2-1)} = q_1 + \frac{C_1}{p_1^2-p^2+ib_1p}. \tag{2}$$

Solving for $\mathfrak{n}^2$, and separating real and imaginary parts, we find

$$n^2(1-\kappa^2) = q_1' + \frac{C_1'(p_1'^2-p^2)}{(p_1'^2-p^2)^2+b_1^2p^2}; \quad 2n^2\kappa = \frac{C_1'b_1p}{(p_1'^2-p^2)^2+b_1^2p^2};$$

$$q_1' = \frac{1+q_1(1-\sigma)}{1-q_1\sigma}; \quad C_1' = \frac{C_1}{(1-q_1\sigma)^2}; \quad p_1'^2 = p_1^2 - \frac{C_1\sigma}{1-q_1\sigma}. \tag{3}$$

We make the following substitutions:—

$$x^2 = \frac{q_1'}{C_1'}p^2; \quad x'^2 = \frac{q_1'}{C_1'}p_1'^2; \quad b^2 = \frac{q_1'}{C_1'}b_1^2;$$

$$\alpha = x^2 - x'^2; \quad \beta = bx. \tag{4}$$

The previous expressions reduce to

$$\frac{n^2(1-\kappa^2)}{q_1'} = 1 - \frac{\alpha}{\alpha^2+\beta^2}; \quad \frac{2n^2\kappa}{q_1'} = \frac{\beta}{\alpha^2+\beta^2}. \tag{5}$$

Equations of this form, with q_1' unity and with different variables, have been investigated by various writers; in studying the extinction curve of $n\kappa$ as a function of wave-length approximate methods have been used. For example, Planck* makes three types according as the maximum of $n\kappa$ is a large, medium, or small number. The last case is the usual approximation which treats β as a large number, the result being a curve for $n\kappa$ symmetrical on both sides of a maximum which occurs near a frequency given by $\alpha = 0$. In the first case, when $n\kappa$ is large, Planck illustrates the unsymmetrical nature of the curve, and after various assumptions, states that its maximum is given by $\beta = \alpha\sqrt{3}$.

Königsberger and Kilching† also point out that the maximum of $n\kappa$ does not occur at the frequency p_1' of the present notation; as a result of an experimental study they conclude that in strongly absorbing substances, in the visible spectrum, the maximum of $n\kappa$ is about 10 $\mu\mu$ from λ_1' towards the shorter wave-lengths. They state that no formula has been derived for the position of the maximum, on account of the complexity of the equations involved.

Without limiting the values of the coefficients we can proceed in the following manner. Solving the equations (5) we have

$$\frac{2n^2}{q_1'} = \left\{1+\frac{1-2\alpha}{\alpha^2+\beta^2}\right\}^{\frac{1}{2}} + 1 - \frac{\alpha}{\alpha^2+\beta^2};$$

$$\frac{2n^2\kappa^2}{q_1'} = \left\{1+\frac{1-2\alpha}{\alpha^2+\beta^2}\right\}^{\frac{1}{2}} - 1 + \frac{\alpha}{\alpha^2+\beta^2};$$

$$\kappa = \frac{\{(\alpha^2+\beta^2-\alpha)^2+\beta^2\}^{\frac{1}{2}} - (\alpha^2+\beta^2-\alpha)}{\beta}. \tag{6}$$

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* M. Planck, 'Sitzungsber. Akad. Berlin,' 1903, vol. 1, p. 480.

† Königsberger and Kilching, 'Ann. der Physik,' 1909, vol. 28, p. 889; also 1910, vol. 32, p. 843.

We see that the maximum of κ occurs when $(\alpha^2+\beta^2-\alpha)/\beta$ has its maximum; that is, when

$$\beta\,(2\alpha-1)\,d\alpha-(\alpha^2-\beta^2-\alpha)\,d\beta = 0,$$
$$3\alpha^2+(4x'^2+b^2-1)\,\alpha+(b^2-2)\,x'^2 = 0.$$

We shall find it convenient to write

$$g = \frac{1}{x'^2};\quad k = \frac{b}{x'};\quad y = \frac{\alpha}{x'^2} = \frac{x^2-x'^2}{x'^2} = \frac{p^2-p_1'^2}{p_1'^2} = \frac{\lambda_1'^2-\lambda^2}{\lambda^2}.$$

The equation for the maximum of κ becomes

$$3y^2+(4+k^2-g)\,y+(k^2-2g) = 0. \tag{7}$$

The only root which comes into consideration is

$$y_\kappa = \tfrac{1}{6}\left[\{(4+k^2-g)^2+12\,(2g-k^2)\}^{\frac{1}{2}}-(4+k^2-g)\right], \tag{8}$$

We shall find that k is small compared with g; if in addition g is small we have often a sufficient approximation in

$$y_\kappa = \tfrac{1}{2}g. \tag{9}$$

For the maximum of $n\kappa$ we differentiate the expression

$$\{1+(1-2\alpha)/(\alpha^2+\beta^2)\}^{\frac{1}{2}}+\alpha/(\alpha^2+\beta^2).$$

Expressing β, $d\alpha$, and $d\beta$ in terms of α and rationalising the equation, we find eventually a quartic equation in α,

$$\begin{aligned} &12\alpha^4+(16x'^2+4b^2-8)\,\alpha^3-(12x'^2+8b^2x'^2+5b^2)\,\alpha^2 \\ &\qquad -(16b^2x'^4+4b^2x'^2+4b^4x'^2+b^4)\,\alpha+(4x'^2-b^2-4b^2x'^2)\,b^2x'^2 = 0. \end{aligned} \tag{10}$$

With values of b and x' such as occur in practice, the coefficients in brackets in this equation are all positive. The equation has extraneous roots which have entered in rationalising the equation for a maximum of $n\kappa$; it is easily seen that it is the smaller positive root which corresponds to a maximum of $n\kappa$. With the same notation as before, the equation becomes

$$\begin{aligned} &12y^4+(16+4k^2-8g)\,y^3-(12g+8k^2+5gk^2)\,y^2 \\ &\qquad -(4+g)\,(4+k^2)\,k^2y+\{4g-(4+g)\,k^2\}\,k^2 = 0. \end{aligned} \tag{11}$$

We can see what the other roots of this equation signify by finding the positions of maximum and minimum refractive index; for this we proceed in the same manner by differentiating

$$\frac{2n^2}{q_1'} = \left(1+\frac{g^2-2gy}{y^2+k^2y+k^2}\right)^{\frac{1}{2}}+1-\frac{gy}{y^2+k^2y+k^2}.$$

After some reduction, one obtains again the same equation (11). The equation has, in practice, four real roots, two positive and two negative. One of the negative roots is clearly greater than 1 numerically; remembering that y is $(\lambda_1'^2-\lambda^2)/\lambda^2$, we see that this root does not enter into consideration. For the other three roots we find the following correspondence:—

Larger positive root (y_n)	Minimum of n,
Smaller positive root $(y_{n\kappa})$...............	Maximum of $n\kappa$,
Negative root, numerically <1, $(y_{n'})$	Maximum of n.

For a first approximation for the smaller roots one can write, as the more important terms of the equation,

$$12gy^2+4k^2(4+g)y-4gk^2 = 0.$$

Hence, approximately,

$$y = \frac{1}{6g}[\pm\{(4+g)^2k^4+12g^2k^2\}^{\frac{1}{2}}-(4+g)k^2]. \tag{12}$$

Taking the radicle with the positive sign, we have $y_{n\kappa}$; while with the negative sign we obtain $y_{n'}$.

For the larger positive root we have approximately

$$12y^4+(16-8g)y^3-12gy^2 = 0,$$

$$y_n = \tfrac{1}{3}[\{(2-g)^2+9g\}^{\frac{1}{2}}-(2-g)]. \tag{13}$$

Of these approximations, that for $y_{n\kappa}$ is generally very good; the others give at least the first significant figure, and one can then obtain the roots from the complete quartic to any desired accuracy.

For the reflective power R we have

$$\mathrm{R} = \frac{(n-1)^2+n^2\kappa^2}{(n+1)^2+n^2\kappa^2}.$$

R is a maximum when $2n/(n^2+n^2\kappa^2+1)$ is a minimum, that is when

$$(n^2-n^2\kappa^2-1)\,dn+2n^2\kappa\,d(n\kappa) = 0,$$

or

$$(n^2+n^2\kappa^2+1)\,dn+2n^3\kappa\,d\kappa = 0. \tag{14}$$

The procedure of the two previous cases leads to an equation which is much too complicated to be of service; in the examples which follow, the maximum of R is found by graphing its values when calculated from the formula. If κ were zero, R (max.) would occur at n (max.). From the above equations, if the absorption is small or n is large, so that $n^2\kappa^2<n^2-1$, R (max.) could occur between n (max.) and $n\kappa$ (max.); otherwise the maximum of R comes between the maxima of κ and $n\kappa$.

For comparison with other formulæ and with experimental data, it is convenient to change from frequency to wave-length.

From (5) we obtain

$$\frac{n^2(1-\kappa^2)}{q_1'} = 1+\frac{g\lambda^2(\lambda^2-\lambda_1'^2)}{(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2}; \quad \frac{2n^2\kappa}{q_1'} = \frac{gg'\lambda^3}{(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2}; \tag{15}$$

where $k = g'/\lambda_1'$, and g and k are the quantities already used in the equations for the maxima.

We may bring together the various wave-lengths which are to be compared. Suppose the dispersion formula is in the form (2), or

$$\frac{1}{\sigma + 1/(\mathfrak{n}^2 - 1)} = q_1 + \frac{C_1\lambda_1^2\lambda^2/4\pi^2c^2}{\lambda^2 - \lambda_1^2 + ib_1\lambda_1^2\lambda/2\pi c}. \tag{16}$$

Then λ_1 is the wave-length of the natural undamped vibrations of a single particle if isolated. λ_1' is an associated wave-length for the medium as a whole, and is the limiting position of maximum absorption when κ is small and the region of absorption is narrow. λ_1' is greater than λ_1, and $\lambda_1'^2$ is equal to $\lambda_1^2\{1 - C_1\lambda_1^2\sigma/4\pi^2c^2(1 - q_1\sigma)\}^{-1}$.

We have, further, the actual maximum of $n\kappa$, which is displaced towards the shorter wave-lengths from λ_1' and is given by $\lambda_1'(1 + y_{n\kappa})^{-\frac{1}{2}}$ in the present notation; similarly we have the maximum of κ and of the reflective power.

It is of interest incidentally to express some of the constants in the manner of Drude, considering the natural vibrations as due to a particle of mass m, charge e; N being the number of such particles per unit volume, and p the number per molecule of the substance.

In (16) above we have $C_1\lambda_1^2/4\pi^2c^2 = 4\pi Ne^2/m$. The equation (16), neglecting absorption, transforms to

$$n^2 = q_1' + \frac{C_1'\lambda_1'^2\lambda^2/4\pi^2c^2}{\lambda^2 - \lambda_1'^2},$$

where q_1' and C_1' are given by (3). Hence we have

$$\frac{g}{\lambda_1'^2} = \frac{C_1'}{4\pi c^2 q_1'} = \frac{C_1\{1 + \sigma(q_1' - 1)\}^2}{4\pi^2c^2q_1'} = \frac{1}{\pi}\,\frac{Ne^2/c^2}{m}\,\frac{\{1 + \sigma(q_1' - 1)\}^2}{q_1'}.$$

Expressing e in electromagnetic units, and with M for the molecular weight and d for the density of the substance, also with 9660 as the value of e/m for hydrogen, we obtain

$$p\frac{e}{m} = \frac{\pi}{9660}\,\frac{M}{d}\,\frac{g}{\lambda_1'^2}\,\frac{q_1'}{\{1 + \sigma(q_1' - 1)\}^2}. \tag{17}$$

Simpler forms which have been used are found by putting σ zero, or by writing q_1' equal to unity.

Iodeosin.

Königsberger and Kilching (*loc. cit.*) have made recently a quantitative study of various strongly absorbing media. It is sufficient to take one example, iodeosin, for which they give the values of n and $n\kappa$ throughout a region of absorption in the visible spectrum; they estimate that this region is associated with one vibrating electron per molecule. We take the values of g, g' and λ_1' which they have calculated from their results, namely,

$\lambda_1' = 5{\cdot}21 \times 10^{-5}$ cm.; $g = 0{\cdot}257$; $g' = 6{\cdot}47 \times 10^{-6}$; $k = g'/\lambda_1' = 0{\cdot}12418$.

From the observed values it is seen that the maximum of $n\kappa$ is 0·82 and occurs at 510 $\mu\mu$. The minimum and maximum of n are at 480 $\mu\mu$ and 550 $\mu\mu$ respectively. The maximum of κ is at about 495 $\mu\mu$; and by calculating and graphing the reflective power, we find its maximum is 18 per cent. at rather less than 540 $\mu\mu$. From equation (8) we have $y_\kappa = 0{\cdot}0963$, and this gives 497 $\mu\mu$ as the maximum of κ. The equation (11) becomes

$$12y^4 + 14{\cdot}006y^3 - 3{\cdot}227y^2 - 0{\cdot}2636y + 0{\cdot}01484 = 0.$$

The approximations of (12) and (13) give for the three roots we need, $-0{\cdot}1$, 0·041, 0·2. From the quartic equation one has more accurately the values $-0{\cdot}095$, 0·0412, 0·24. For the minimum and maximum of n these give 468 and 548 $\mu\mu$ respectively; and for the maximum of $n\kappa$ we find 510 $\mu\mu$.

These calculations agree well with the observed values, except for the minimum of n; of course from the method of calculation in this case any considerable lack of agreement is due to n and $n\kappa$ not being represented with sufficient accuracy by simple dispersion formulæ with the above values of the constants. Using a Lorentz type of formula, Königsberger and Kilching calculate λ_1 for the natural undamped vibrations as 497 $\mu\mu$. We have then the following series of wave-lengths:—

λ_1 and λ_κ.	$\lambda_{n\kappa}$.	λ_1'.	λ_R.
497	510	520	540

We notice that $\lambda_R > \lambda_1'$ in this case, corresponding with the fact that in this region $n^2\kappa^2 < n^2 - 1$, as in equation (14).

Carbon Disulphide.

We consider now a substance for which quantitative measurements of the selective absorption are not available; we confine our attention to the principal region in the ultra-violet. In a previous paper various dispersion formulæ for CS_2 were examined; using values of the refractive index given by Flatow, namely:—

λ	441	508	589
n	1·67180	1·64586	1·62806,

one obtained a formula,

$$\frac{n^2-1}{n^2+2} = q + \frac{C}{\lambda^2 - \lambda_1^2}, \qquad (18)$$

with

$q = 0{\cdot}33567$; $C = 0{\cdot}005843$; $\lambda_1^2 = 0{\cdot}04338$; $\lambda_1 = 208\ \mu\mu$

This is not given as a complete formula; it ignores, for example, the minor region of absorption near 325 $\mu\mu$, but it suffices for the present purpose. We have to introduce a suitable value for g', denoting absorption, and then work out the various maxima. In order to do this, we first transform (18) to the form

$$\frac{n^2}{q_1'} = 1+\frac{g\lambda^2}{\lambda^2-\lambda_1'^2}, \tag{19}$$

so that we can compare it with the complete formulæ in (15). Making the calculations we find

$$q_1' = 1{\cdot}7544; \quad g = 0{\cdot}434; \quad \lambda_1'^2 = 5{\cdot}217\times 10^{-10}; \quad \lambda_1' = 2{\cdot}284\times 10^{-5}\text{ cm.}$$

From (17), with σ equal to $\frac{1}{3}$, we have

$$p\frac{e}{m} = \frac{\pi}{9660}\frac{\text{M}}{d}\frac{g}{\lambda_1'^2}\frac{9q_1'}{(q_1'+2)^2} = 1{\cdot}79\times 10^7.$$

This indicates one electron per molecule, in contrast with Drude's calculation, which gave two electrons per molecule. In Drude's form σ is zero; if we write $n^2 = \Sigma m'\lambda^2/(\lambda^2-\lambda'^2)$ and use Flatow's values of m' and λ' for CS_2 at 20°, we have

$$p\frac{e}{m} = \frac{\pi}{9660}\frac{\text{M}}{d}\frac{m'}{\lambda'^2} = 2\times 1{\cdot}53\times 10^7.$$

We have now to introduce a suitable value of g', so that (19) is replaced by the two equations (15). A simple way would be available if we knew the reflective power R at λ_1'; for at this place we have $n^2(1-\kappa^2) = q_1'$ and $2n^2\kappa = q_1'g\lambda_1'/g' = q_1'g/k$.

Another method would be to use a knowledge of the position of any of the maxima, for the quartic equation (11) in y is a quadratic for k. In the present case we adopt another method. Retaining the above values of q_1', g and λ_1' unaltered, for simplicity, means that we regard κ as inappreciable at the wave-lengths at which these constants were determined. Now the index n is given by Flatow as 2·08884 at a wave-length 267 $\mu\mu$. The formula (19) gives a calculated value much too high, and by trial we estimate g' so as to reduce this value nearer to the observed one at 267, without having much effect at 441 $\mu\mu$.

It is sufficient to take $g' = 2{\cdot}284\times 10^{-6}$, that is $k = 0{\cdot}1$; we obtain then a calculated index of 2·0904 at 267 $\mu\mu$. This value of g' is probably of the right order of magnitude, and we proceed with the constants of (15) so determined.

For the maximum of κ we find $y_\kappa = 0{\cdot}205$, and $\lambda_\kappa = 208\,\mu\mu$. We have also $\lambda' = 208\,\mu\mu$; in this case, as in the previous one, the maximum of κ coincides practically with the wave-length λ_1. The quartic equation becomes

$$12y^4+12{\cdot}568y^3-5{\cdot}3097y^2-0{\cdot}1778y+0{\cdot}01693 = 0.$$

The roots required are $-0{\cdot}066$, $0{\cdot}044$, and $0{\cdot}34$. Hence $\lambda_{n\kappa}$ is 223·4 $\mu\mu$; and the minimum and maximum of n are at 198 and 236·4 respectively. In fig. 1 the values of n and $n\kappa$ have been graphed from the formulæ: one notices the unsymmetrical nature of the curves, $n\kappa$ descending more steeply towards the longer wave-lengths, and the maximum of n being sharper than the minimum. From the calculated values one obtains the curve of reflective power R; its maximum is about 40 per cent. at 215 $\mu\mu$, a smaller wave-length than for the maximum of $n\kappa$. The only experimental result available in this respect is an observation by Flatow. Using a method of repeated reflection from carbon disulphide pressed between plates of quartz or fluorspar, he concluded that the maximum of selective reflection was in the vicinity of 230 $\mu\mu$. One might apply certain corrections allowing for the presence of the quartz plate, for instance, by using the relative index of refraction; but any such correction would tend to increase slightly the above estimate. Possibly the absorption coefficients are too large in the formulæ we have used; but in any case further observations by means of residual rays in the ultra-violet are desirable.

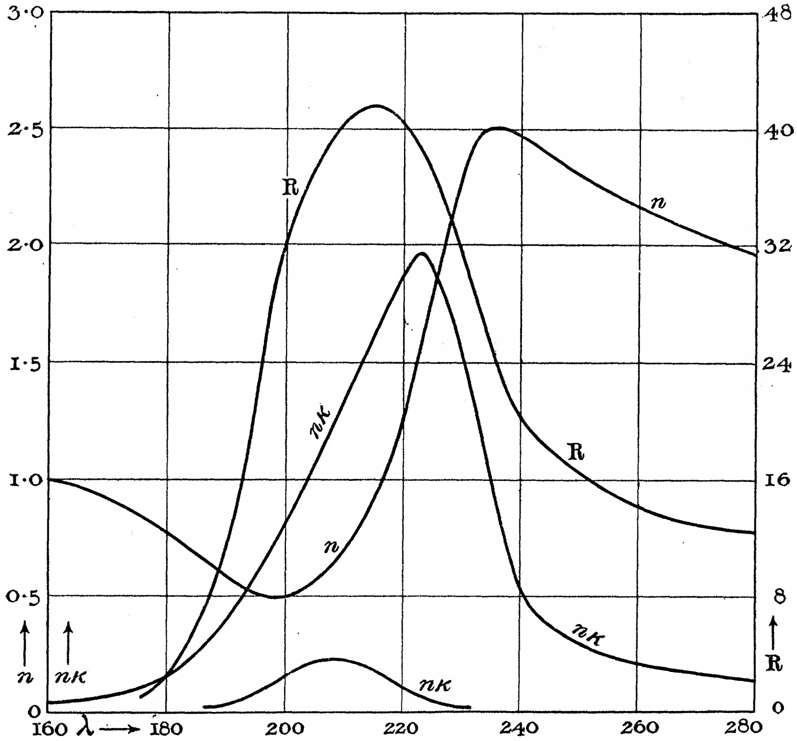

Fig. 1.

There is more satisfactory agreement in the case of the absorption maximum. The observations refer to a capillary layer of a solution of one part by volume of carbon disulphide in ten parts of alcohol; it was found that almost complete absorption occurred from about 190 to 228 $\mu\mu$, with a mean position of 210 $\mu\mu$.

We must modify the constants so as to make the formulæ suitable for such a solution. This problem deserves fuller investigation, but for the present we use the following method of estimating the effect. We assume that $(n^2-1)/(n^2+2)$ is additive, so that, for volumes V_1 and V_2 of two substances making a total volume V of solution, we have

$$\frac{n^2-1}{n^2+2} = \frac{V_1}{V}\frac{n_1^2-1}{n_1^2+2} + \frac{V_2}{V}\frac{n_2^2-1}{n_2^2+2}.$$

Instead of equation (18) we have a similar one with different constants, the transformation to the form (19) giving the scheme

$$\begin{gathered}
n^2(1-\kappa^2) = q_2 + \frac{C_2\lambda^2(\lambda^2-\lambda_1'^2)}{(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2}; \qquad 2n^2\kappa = \frac{C_2 g'\lambda^3}{(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2}; \\
q_2 = q_1' - C_1'/\lambda_1'^2; \quad C_2 = C_1'/\lambda_1'^2; \quad q_1' = (1+2q_1)/(1-q_1); \\
C_1' = 3C_1/(1-q_1)^2; \quad \lambda_1'^2 = \lambda_1^2 + C_1/(1-q_1); \quad C_1 = V_1C/V; \\
q_1 = \frac{V_1}{V}q + \frac{V_2}{V}\frac{n_2^2-1}{n_2^2+2}. \qquad (20)
\end{gathered}$$

In the present case we may ignore any absorption due to the solvent, and also assume n_2 as constant (1·43) in the range in question.

For the dissolved substance we take the values of q, C, and λ_1 the same as before, in (18); taking the volumes in the ratio of 1 to 10, we find the values

$$\lambda_1' = 210\,\mu\mu; \quad q_2 = 2{\cdot}016; \quad g = C_2/q_2 = 0{\cdot}033.$$

If we give k the same value as before, we have $k = 0{\cdot}1$ and $g' = 2{\cdot}1 . 10^{-6}$. From equation (12) we find $y_{n\kappa} = 0{\cdot}008$ and consequently the maximum of $n\kappa$ is at the wave-length 209 $\mu\mu$. This agrees well with the observed mean position of 210 $\mu\mu$ for the solution. The curve for $n\kappa$ for the solution has been graphed and is shown in fig. 1.

Rock Salt.

For this substance we consider first Maclaurin's dispersion formula,*

$$\frac{n^2-1}{n^2+a} = \frac{K-1}{K+a} + \frac{C_1}{\lambda^2-\lambda_1^2} + \frac{C_2}{\lambda^2-\lambda_2^2},$$

$$\begin{aligned}
\lambda_1^2 &= 0{\cdot}0160074, & \lambda_2^2 &= 2632{\cdot}14, \\
C_1 &= 0{\cdot}00191605, & C_2 &= 683{\cdot}816, \\
a &= 5{\cdot}51, & K &= 5{\cdot}9, \\
\lambda_1 &= 0{\cdot}12652\,\mu. & \lambda_2 &= 51{\cdot}3\,\mu.
\end{aligned}$$

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* 'Roy. Soc. Proc.,' A, 1908, vol. 81, p. 367.

For this form, with a general instead of equal to 2, we can easily modify the previous expressions for reduction to the required form. We find in the vicinity of λ_1, with the same notation as in (19),

$$q_1' = 1{\cdot}3422\,; \quad g = 0{\cdot}7359\,; \quad \lambda_1' = 0{\cdot}1353\,\mu.$$

For the value of $p\,.\,e/m$ from (17) we have $M = 58{\cdot}5$, $d = 2{\cdot}28$, and $\sigma = 1/6{\cdot}51$; we find $p\,.\,e/m = 4{\cdot}06 \times 10^7$. This might be interpreted as two electrons per molecule. Drude's calculation gave a value of $4 \times 1{\cdot}57 \times 10^7$.

To estimate the maximum of $n\kappa$ we take $k = 0{\cdot}1$, so that $g' = 1{\cdot}353\,.\,10^{-6}$. We obtain $y_{n\kappa} = 0{\cdot}048$, and the maximum of $n\kappa$ occurs at $0{\cdot}1322\,\mu$. The reflective power has not been calculated in this case; apart from this we have the sequence $\lambda_1 = 0{\cdot}1265\,\mu$, $\lambda_{n\kappa} = 0{\cdot}1322\,\mu$, and $\lambda_1' = 0{\cdot}1353\,\mu$.

We consider now more fully the region in the infra-red. Making similar calculations, we find

$$q_2' = 2{\cdot}332\,; \quad g = 1{\cdot}53\,; \quad \lambda_2 = 513 \times 10^{-5}\,\text{cm.}\,; \quad \lambda_2' = 619 \times 10^{-5}\,\text{cm.}$$

If we calculate pe/m in this case we find a value 536, indicating a vibrating particle of mass comparable with that of the molecule, if we hold to the simple interpretation.

We have no direct guide to an estimate of g'. We keep to the previous method of putting $k = g'/\lambda_2' = 0{\cdot}1$; we shall find that this gives values of the reflective power similar to those obtained by experiment. Reverting to the primitive form of the dispersion formula in (1), it appears that making k constant is equivalent to making the quantity b_1 vary directly as the natural frequency; b_1 appears in the equation of the vibrating particle in the term $b_1 dx/dt$, a term which is frequently written in the form $b_1 p_1 dx/dt$.

Having assigned the values of the constants, we calculate the various maxima. We find $y_\kappa = 0{\cdot}676$ and $\lambda_\kappa = 47{\cdot}8\,\mu$.

The quartic equation becomes

$$12y^4 + 3{\cdot}8y^3 - 18{\cdot}516y^2 - 0{\cdot}2217y + 0{\cdot}06065 = 0.$$

The required roots are $0{\cdot}052$, $1{\cdot}09$, and $-0{\cdot}063$. These give $\lambda_{n\kappa} = 60{\cdot}3\,\mu$, and the minimum and maximum of n at $42{\cdot}8\,\mu$ and $63{\cdot}9\,\mu$ respectively.

Values of n and $n\kappa$ have been calculated and the curves are shown in fig. 2; on account of the larger magnitudes the unsymmetrical features are very marked. The values of the reflective power R have also been graphed; we find a maximum of about 76 per cent. at $52\,\mu$. Recent experiments with residual rays give a double maximum with a mean position of $52{\cdot}3\,\mu$. Other observations have given the following estimated values of R in percentages:—$1{\cdot}7$ at $23{\cdot}7\,\mu$, $81{\cdot}5$ at $51{\cdot}2\,\mu$, $52{\cdot}6$ at $61{\cdot}1\,\mu$, $25{\cdot}8$ at $82{\cdot}3\,\mu$, and 20·3 at 108 μ; these have been marked by circles in fig. 2, and one sees that the calculated curves agree well in a general way with these results. Probably the value of g' is too large, and one might obtain a less rounded curve by taking a smaller value, but one does not lay much stress on actual agreement, because the curves are meant to be illustrative in the first instance.

With the above formula, Maclaurin identified λ_2 with the position of maximum reflection obtained by residual rays, taking that to be 51·3 μ. We have seen that, compared with the simpler form of dispersion formula, the wave-length λ_1 is replaced by λ_1', equal to 61·9 μ, which would be the position of maximum absorption if that were small. Putting in a more suitable value for the absorption, we have found that the maximum is at 60·3 μ, only slightly displaced to the shorter wave-length from λ_1'; however, under the same conditions we find that the maximum of selective reflection occurs at 52 μ.

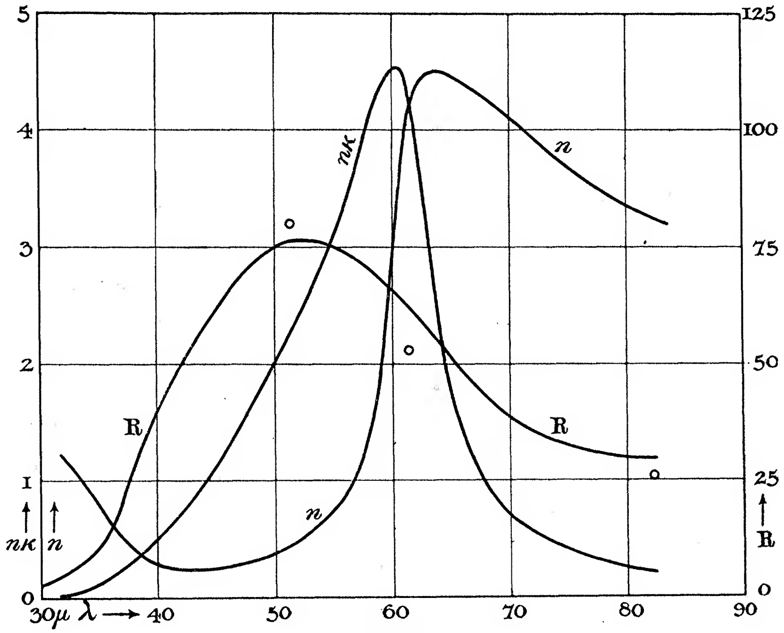

Fig. 2.

Similar calculations could be made for any of the dispersion formulæ which have been given for rock salt. These are generally in the form $n^2-1 = \Sigma C_1/(\lambda^2-\lambda_1^2)$, that is, σ is zero and λ_1' coincides with λ_1. Martens in making such a formula put the wave-length λ_r for the infra-red equal to the observed position of maximum reflection, but we have seen that when absorption coefficients are introduced the maximum of R occurs at a considerably less wave-length than the λ_r of the formula. Paschen* determined λ_r directly from the values of the refractive index, and claims that his formula with $\lambda_r = 60\mu$ represents the dispersion better, in spite of apparent disagreement with the reflection maximum. If we put Paschen's formula into the form used above, for the vicinity of $60\,\mu$, we find $q_2' = 2{\cdot}33$, $g = 1{\cdot}44$, and $\lambda_2' = 60\,\mu$. These values are not much different from those of Maclaurin's formula when expressed similarly. It is unnecessary to repeat the calculations; if we introduced a quantity g' as before, we should find the maximum of reflective power to be in the neighbourhood of $50\,\mu$. It seems probable then that Paschen's formula, when interpreted aright, does not disagree with the results of reflection experiments.

Absorption in Vapours.

The absorption in the previous cases is enormously larger than that of gases and vapours, so that the differences between the various maxima in the latter are very minute and generally quite beyond the limits of observation. For dense mercury vapour R. W. Wood† has been able to observe selective reflection, with the interesting result that the maximum reflective power occurs at about one Ångström unit towards the shorter wave-lengths from the absorption maximum. The particular line in question is near 2536 Å.U., and it shows powerful anomalous dispersion. The vapour was contained in a fused quartz tube, and Wood suggests that the displacement is entirely a spurious effect due to the relative index of refraction of quartz and the vapour being nearly unity on the side of the longer wave-lengths but quite large towards the shorter wave-lengths from the absorption line. There are no data available for the dispersion of mercury vapour by which one might test this numerically. As a similar example we use the values given by Wood for dense sodium vapour; for a single mean absorption at 5893 Å.U., the dispersion formula is

$$n^2 = 1 + \frac{g\lambda^2}{\lambda^2 - \lambda_1^2},$$

with $g = 5{\cdot}5 \times 10^{-5}$, $\lambda_1 = 5{\cdot}893 \times 10^{-5}$ cm.

This formula is only approximate; to obtain any approach to observed values near the D-lines, Wood alters the value of λ_1. However, one can use it as an example of the numerical magnitudes of the quantities. It has been estimated that in less dense sodium vapour the logarithmic decrement of the natural vibrations is of the order 10^{-5}; in the present case we shall take $k = g'/\lambda_1 = 4 \times 10^{-5}$, a value which gives moderate reflective powers. From the formula (12) we find that the maximum of $n\kappa$ is at less than 5893 by about 0·014 Å.U. Working out values of n and $n\kappa$ we obtain a maximum reflective power of 9·6 per cent. at 5892·9 Å.U. If we divide the values of n by a mean value for the index of quartz, say 1·55, we can graph the reflective power taking account of the effect of the wall of the tube; this shifts the maximum further to the shorter wave-lengths by about 0·1 Å.U. We obtain thus a total displacement of about 0·2 Å.U., of which one-half is due to the wall of the tube. This displacement is several times smaller than that observed in mercury vapour, but there are certain possibilities to be noticed. In sodium vapour with the above value of g it has been estimated that there is not more than one vibrating electron for every 12 molecules; in mercury vapour the ultra-violet line showed very strong anomalous dispersion, and is probably a more dominant natural vibration with a larger value of g. In addition, the absorption extended over several Ångström units. Hence the conclusion is that while the displacement observed by Wood may be exaggerated by the presence of the quartz wall, it is probably in part a true effect—a displacement of the reflection maximum from the absorption maximum towards the shorter wave-lengths.

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* F. Paschen, 'Ann. der Physik,' 26, p. 130, 1908.

† R. W. Wood, 'Phil. Mag.,' 18, p. 187, 1909.